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TECHNETIUM MEASUREMENT

O. H. Howard

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Prepared by Union Carbide Corporation--Nuclear Division, operating contractor for the U.S. Department of Energy under U.S. Government Contract No. W-7405-eng-26.

INTRODUCTION

Technetium-99 (hereafter designated Tc) is measured in various gaseous, liquid, and solid materials at the ORGDP. Gases analyzed include uranium hexafluoride (UF_6), air (work-area and environment), and the vent gas from the Purge Cascade Scrubber. Liquids analyzed include water (surface and Effluent), the Purge Cascade Scrubber solution, the waste acid (raffinate) from the decontamination operations, and urine. Solids analyzed include uranium oxide (U_3O_8) from scrap recovery, trapping materials (Al_2O_3, NaF, MgF_2), soil, solid waste from the Purge Cascade Scrubber, and barrier.

General methods of analysis include radiochemical[1], spectrochemical[2], and colorimetric[3]. However, because of the generally low levels of Tc, most of the analyses are radiochemical. Currently, procedures involving liquid-scintillation beta spectrometry (LSBS) are used. Any uranium and its beta-emitting daughters are either separated as the insoluble hydroxides, by solvent extraction of the Tc, or the Tc result is corrected for the beta emissions of uranium daughters. Other interfering elements, e.g. nickel, are separated as insoluble hydroxides. For the LSBS measurement, 1 or 2 ml of the preapred sample solution is mixed with 15 ml of a scintillator solution, and the beta emissions are counted for 20 min. A measured amount of a Tc standard solution containing 10,000 to 20,000 dpm of Tc is then added and the mixture is counted for 1 min to calibrate the spectrometer and correct for any quenching effect. From these data and any aliquot, dilution, and recovery or other correction factors, the activity of Tc in the sample is calculated.

BRIEFS OF PROCEDURES

URANIUM HEXAFLUORIDE

Uranium Hexafluoride is sampled in the liquid state[4]. A subsample is hydrolyzed. Boric acid, potassium carbonate, and hydrogen peroxide are added, and the Tc is extracted with methyl ethyl ketone[1]. The Tc is back-extracted into water and measured by LSBS. An average recovery factor of approximately 80% is applied, as determined by analysis of known samples. The detection limit is 75 pCi/gU.

URANIUM OXIDE (U_3O_8)

Uranium oxide, from the scrap recovery facility, is dissolved in nitric acid. Sodium hydroxide is added to precipitate uranyl hydroxide. The solution is centrifuged, and the Tc in the supernate is measured by LSBS. The detection limit is 75 pCi/gU.

AIR

Air in the work area or environment is sampled through paper filters, as described in the Health and Environmental Sections. The filters are leached with nitric acid. The beta activity in a portion of the leach solution is measured by LSBS, and the total beta activity in the air filter is calculated.

The uranium in a second portion of the leach solution is measured by alpha spectrometry. The alpha activity in the air filter is multiplied by a beta/alpha factor (2.5), previously determined by measuring the beta activity of uranium by LSBS. The product is subtracted from the beta activity in the air filter, and the net activity is calculated as Tc. The detection limit is 150 pCi per filter.

VENT GAS

Vent gas from the Purge Cascade Scrubber, which is discharged to the atmosphere, is sampled by passing the gas through two impingers in series, each impinger containing 300 ml of 1 wt % potassium hydroxide solution. The flow rate is 100 ft^3 (2.83 m^3) per 24 h. One 3-day sample per week is taken for a total sample of 300 ft^3 (8.49 m^3). The solution is acidified with nitric acid, sodium persulfate is added to ensure Tc^{7+} oxidation state, and ferric nitrate is added as a carrier for trace uranium. The solution is made basic with sodium hydroxide, centrifuged, and the beta activity of the supernate is measured by LSBS. The detection limit is 2 pCi/ft^3 (70.67 pCi/m^3) of vent gas.

WATER

Effluent and surface waters are sampled, as described in the Environmental Section. A 2-l sample is taken for analysis. Nitric acid and sodium persulfate are added to ensure dissolution of the Tc and oxidation to Tc^{7+}.

The solution is then concentrated approximately 10-fold by evaporation. Ferric nitrate is added and then sodium hydroxide, precipitating ferric hydroxide which serves as a carrier for small amounts of uranium and its beta-emitting daughters. The solution is centrifuged, and the beta activity of the supernate is measured by LSBS. The concentration of Tc in the water is calculated assuming that all of the measured activity is due to Tc. The detection limit is 3 pCi/ml.

In the absence of beta emitters other than Tc, water may be analyzed by direct LSBS.

DECONTAMINATING SOLUTION

To the waste nitric acid (raffinate) from the decontaminating facility, sodium persulfate is added, and the solution is made basic with sodium hydroxide. After centrifugation to remove insoluble hydroxides, including uranium and its beta-emitting daughters, the Tc is measured in the supernate by LSBS. The detection limit is 10 pCi/ml.

PURGE CASCADE SCRUBBER SOLUTION

This potassium hydroxide solution is acidified with nitric acid and sodium persulfate is added to ensure dissolution of Tc and oxidation to Tc^{7+}. Lanthanum nitrate is added to combine with fluoride. Finally, ferric nitrate is added, the solution is made basic with sodium hydroxide and centrifuged. Tc in the supernate is measured by LSBS. The detection limit is 10 pCi/ml.

URINE

A urine sampling program is conducted as described in the Health Section. The Tc activity is determined by mixing 1 ml of sample with 15 ml of liquid scintillator and measuring the beta emission by LSBS. The beta activity is corrected for any beta activity due to uranium, as determined from a separate, routine alpha activity measurement[5] and a previously determined beta/alpha factor for uranium by LSBS. The corrected beta activity is presumed to be due to Tc. The detection limit is 3 pCi/ml.

SOIL AND SEDIMENT

Soil and sediment are sampled as described in the Environmental Section. The material is dried, blended, and leached with nitric acid. Sodium persulfate is added to ensure oxidation of the Tc to Tc^{7+}. Ferric nitrate is added to the leach solution which is then made basic with sodium hydroxide and centrifuged. The beta activity of the supernate, assumed to be due to Tc since any uranium and its beta-emitting daughters are precipitated as hydroxides, is measured by LSBS. The detection limit is 15 pCi/g.

BARRIER

Samples of barrier tubing are taken from converters upon removal from the cascade and prior to decontamination. For measurement of Tc, a sample is dissolved in nitric acid, the Tc is oxidized to Tc^{7+} with sodium persulfate, the fluoride is reacted with boric acid and the nickel and uranium are precipitated with sodium hydroxide. The Tc in the supernate is measured

by LSBS. The detection limit is 60 pCi/g.

CHEMICAL TRAPPING MATERIALS AND OTHER SOLID WASTE

Aluminum oxide, sodium fluoride, and magnesium fluoride, which have been used to trap uranium hexafluoride, and Purge Cascade Scrubber waste are leached with nitric acid containing sodium persulfate. Fluoride is removed with Lanthanum. Ferric nitrate is added, the solution is made basic with sodium hydroxide, centrifuged, and the Tc in the supernate is measured by LSBS. The detection limit is 10 pCi/g.

PRECISION AND ACCURACY

Results and precisions of analyses of the three gaseous diffusion plant laboratories on two effluent water samples are as follows:

	Tc, µg/l		
Sample No.	ORGDP	PGDP	GAT
001 (11-17-77)	0.90 ± 0.04*	0.71 ± 0.005	0.67 ± 0.069
X701B (11-17-77)	11.4 ± 0.2	7.8 ± 0.13	10.2 ± 0.84

*Standard deviation

The relative differences among the results by the three laboratories range from 6% to 38%.

Five analyses of a spiked solution of a barrier sample gave a rel std dev of ±3% and a recovery of 100%. Analyses of a series of synthetic air filter samples containing 8000 pCi of Tc and 150 to 1800 pCi of uranium gave a rel std dev of ±4% and a recovery of 103%.

SUMMARY

Technetium-99 is measured in various gaseous, liquid and solid materials at the ORGDP, principally by liquid-scintillation beta spectrometry after appropriate sample preparation. The detection limit is 3 pCi and the relative standard deviation is less than ±10%. Relative differences with other laboratories on effluent waters ranged from 11% to 38%, at 1 to 10 µg Tc/1.

WORK TO BE DONE

Document Procedures.

Develop procedure for vegetation.

Prepare, analyze and document measurement controls for all procedures.

ACKNOWLEDGEMENT

W. T. Mullins, Supervisor of the Radioanalysis Laboratory, and his staff performed the Tc analyses. Mullins and T. L. Rucker developed the analytical procedures.

REFERENCES

1. Analytical Procedure Number 2224, Technical Services Division, ORGDP.

2. Analytical Procedure Number 2.705.09.01, Technical Services Division, ORGDP.

3. Howard, O. H. and C. W. Weber, Analytical Chemistry, 34, 530 (1962).

4. Procedures for Handling and Analysis of Uranium Hexafluoride, Procedures ~~X1.3~~ X-1.3, and X-2.1, Department of Energy, ORO-671-1 & 2.

5. Analytical Procedure Number 2205, Technical Services Division, ORGDP.